I. METHOXYSTILBENEDIOLS
II. ISOMERIC BROMO-1,2-DIMESITYL-1-PROPEN-1-OLS

BY
PAUL BURKE WELLDON
A.B., Dartmouth College, 1937
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AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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I. METHOXYSTILBENEDIOLS

Introduction

The cause of the remarkable permanence of the diarylacetylene glycols[1] appears to be closely related to the so-called ortho effect. It is also possible that the aromatic character of the rings exerts a profound influence on the behavior of the enediols. The methoxyl group is known to change the nature of the benzene ring markedly; it was the purpose of this investigation to prepare methoxystilbenediols for comparison with other members of the series.

Experimental and Discussion of Results

3-Methoxymesitoyl chloride (I) was synthesized as follows: mesityl methyl ether → 3-methoxybromomesitylene → 3-methoxymesitoic acid → I. When the acid chloride (I) was subjected to a reductive coupling reaction using the binary mixture, Mg + MgI_2,[2] the products were *cis* 1,2-di-(3-methoxymesityl)-acetylene glycol (55 per cent yield), 3,3′-dimethoxymesitil (26 per cent yield), and traces of a white solid having the composition of 3,3′-dimethoxydimesitylacetylene. A similar acetylene had been encountered earlier in the isodurene series.[3]

Prolonged low pressure catalytic reduction of the benzil in the presence of a trace of piperidine yielded the higher-melting *trans* enediol. The *cis* enediol could also be produced by rapid reduction in the presence of a trace of acetic acid. These enediols were similar in stability to the corresponding 1,2-diarylacetylene glycols[1] containing no methoxyl groups, and possessed the same remarkable properties. The *cis* form was appreciably oxidized to the yellow benzil by twenty minutes of contact with air; the *trans* form remained colorless after two weeks of such exposure. Neither form showed any tendency to ketonize spontaneously; in fact, various catalytic treatments failed to effect such an isomerization.

Diacetates of both the *cis* and *trans* enediols were prepared. The action of phosgene on the *cis* enediol merely caused its isomerization to the *trans* form. High pressure hydrogenation of 3,3′-dimethoxymesitil could be made to produce either 1,2-di-(3-methoxymesityl)-ethane or 1,2-di-(3-methoxymesityl)-ethylene glycol.

Reduction of 2,2′,6,6′-tetramethylanisil (previously prepared by Corse[4]) using 40 lbs. pressure of hydrogen and Raney nickel as catalyst produced the white, solid enediol, 1,2-di-(4-methoxy-2,6-xylyl)-acetylene glycol. This compound was the most unstable of any of the stilbenediols actually isolated; it was oxidized to the corresponding diketone immediately upon exposure to air. Its extreme instability may be attributed to the activating effect of the the methoxyl groups in the *para* positions, although such groups in the *meta* positions do not exert any appreciable effect on the stability of enediols. Similar effects due to the position of substituents were observed to a less marked degree in the bromostilbenediols.[5]

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II. ISOMERIC BROMO-1,2-DIMESITYL-1-PROPEN-1-OLS

Introduction

In an effort to relate the remarkable stability of 1,2-diaryl-1-propen-1-ols[1] to structural features, it seemed desirable to study corresponding enols containing bromine substituents. The present research has been concerned with the preparation of such compounds, and the rather surprising experimental results incidental to the synthesis.

Experimental and Discussion of Results

1-(3-Bromomesityl)-2-mesityl-1-propen-1-ol (I) had

previously been made in solution by Lindsey[2]; his synthesis was repeated as follows: 3-bromomesitoyl chloride + ∝[2]-isodurylmagnesium chloride → 3′-bromodesoxymesitoin → 3-bromomesityl ∝-mesitylvinyl ketone → I. Because the yields of 3′-bromodesoxymesitoin were very low, an effort was made to find a more satisfactory method of preparation. The Friedel-Crafts reaction between mesitylacetyl chloride and bromomesitylene produced in good yields a compound of the composition of 3′-bromodesoxymesitoin but not identical with it. This anomalous product was subsequently shown to be 3-bromodesoxymesitoin, the bromine atom having migrated from one ring to the other during the reaction.

The identity of the new bromodesoxymesitoin was established by converting it to 1-mesityl-2-(3-bromomesityl)-1-propen-1-ol through the intermediate vinyl ketone, mesityl ∝-(3-bromomesityl)-vinyl ketone. Oxidative cleavage of this new enol by the recently discovered method of Fuson and Rachlin[3] produced mesitol and 3-bromoacetomesitylene; similar oxidation of the original enol (I) gave 3-bromomesitol and acetomesitylene. The position of the bromine atom in each isomer was thus fixed.

The structure of 3-bromodesoxymesitoin was also confirmed by an independent synthesis. It was obtained in satisfactory yield by condensing 3-bromomesitylacetyl chloride with mesitylene.

The remarkable migration involved in the Friedel-Crafts reaction must occur at some intermediate point in the condensation, for 3′-bromodesoxymesitoin did not undergo isomerization when treated with aluminum chloride.

Both of the isomeric bromo-1,2-dimesityl-1-propen-1-ols were found to be considerably more unstable than similar vinyl alcohols[1] containing no halogen substituent.

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VITA

The author was born in Nashua, New Hampshire, on May 10, 1916. He attended the public schools of that city and of Manchester, New Hampshire, and was graduated from Manchester High School (Central) in 1933. In the fall of 1933, he entered Dartmouth College, and received the degree of Bachelor of Arts in June, 1937. From September, 1937, until June, 1939, he served as instructor of chemistry at Dartmouth College, where he received the degree of Master of Arts in June, 1939. In September, 1939, he enrolled in the University of Illinois, where he held a Cramer Fellowship from 1939 to 1940 and a University Fellowship from 1940 to 1942.

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